# THE DETERMINATION OF THE SOLUBILITY OF

NATURAL GASES IN CRUDE OILS

Thesis by B.H.Sage

In partial fulfillment of the requirements for the degree of Master of Science.

California Institute of Technology

Pasadena California

- 1931 -

#### Introduction

Methods of increasing the yield of crude oil have been major problems of the oil industry in recent years. It was soon established that the physical properties of the crude oil play an important part in its recovery. Viscosity, surface tension and density are perhaps the most important properties in this connection.

The solution of natural gas in the oil causes a marked decrease in its viscosity and surface tension. Before an intelligent study of this decrease can be made, a knowledge of the influence of pressure and temperature on the solubility of gas is desirable. The work of this research was devoted to the development and construction of an apparatus suitable for measuring the solubility of natural gases in crude oil at such temperatures and pressures as to duplicate most of the conditions found in nature.

# Previous work:

The available information on the high pressure solubility of any gases in liquids has been meager until the last year. Dow and Calkins<sup>1</sup> determined the solubility of air and one very dry natural gas in three samples of crude oil and one sample of kerosene. The maximum pressure employed was  $350 \ \#/"$  (pounds per square inch). The effect of temperature on the solubility was determined to some degree. An attempt was also made to measure the change in viscosity, but due to the apparatus used the results are questionable. There was some description of experimental methods.

Beecher and Parkhurst<sup>2</sup> made numerous determinations of the solubility of natural gases in crude oils up to about 300 #/" and found that in the range studied the amount of gas dissolved was proportional to the pressure. At 200 #/" the solubility of a relatively dry natural gas in different crudes varied from 31 to 46 cubic feet per barrel, while that of carbon dioxide was about 100, air and hydrogen being 10 and 7 respectively. The solubility at  $110^{\circ}$ F was about three quarters

1 Dow and Calkins Bureau of Mines Report. p (101) 1926 2 Beecher and Parkhurst Petroleum Development and Technology p. 61, 1926 of that at  $70^{\circ}$  F. In this work the oil was saturated with gas and the amount of gas recovered from a known volume of the mixture was determined. The possibility of a change in volume occurring was suggested, but no heed was taken of it in the calculation. They also made numerous determinations on the change in viscosity and surface tension with dissolved gas. The maximum pressure used in the latter work was 200 #/". They found a decrease in viscosity of about 15% and a decrease in surface tension of 12%.

Mills and Heithecker<sup>3</sup> determined the solubility of a sample of natural gas in three crudes up to 1,000 #/". The gas used contained about 12% ethane. In this work, as in most of the previous work, the oil was first saturated with the gas and the volume of gas recovered upon release of pressure was determined for a sample of known volume. Analyses of the recovered gases differed from that of the original gas, indicating selective absorption. They noted that the volumes of the crudes did not quite return to their original values.

Larsen and Black<sup>4</sup> studied the solubility of nitrogen and hydrogen in liquid ammonia up to 150 atmospheres.

3 Mills and Heithecker Bureau of Mines p. 101, 1928
4 Larsen and Black J.I.E.C. 17,715, 1925

They found that Henry's law was valid within experimental error. There was no description of the method employed.

In Seidel's treatise entitled "Solubilities" the solubility of carbon dioxide in water up to about 25 atmospheres is given. It is found that the straight line relation holds only to about 5 atmospheres. Applying the gas law corrections, only makes the deviation greater. In general it can be said that where any chemical combination takes place between the solute and the solvent Henry's law is invalid.

Frolich<sup>5</sup> and three co-workers during the past year have added more to our knowledge of solubilities at relatively high pressure than any others. They studied the solubility of hydrogen, nitrogen, methane, hydrogen sulphide, and oxygen in gas oil, carbon tetrachloride, ethyl alcohol, heavy naptha (density 0.805), water and pentane. The work was carried to a maximum pressure of about 2,500 #/". The results were obtained in a manner similar to that employed by Mills and Heithecker. The accuracy of the results is about plus or minus 5 percent. All of the work was done at 25 C. They found that all of the difficultly condensable gases obeyed Henry's law within experimental error. However,

5 Frolich J.I.E.C. 548 - 23 - 1931

methane showed a greater solubility at higher pressures than that called for by the straight line relation. The work on the easily condensable gases was uncertain, but it was concluded that they did not follow Henry's law.

# Present Methods

In reviewing the previous work, one notices three facts. Except in one case, the work did not go over 1,000 #/". All of the work was done by the same general method; that is, by measuring the gas evolved from a known volume of the solution. There has been no study of the effect of temperature for pressures over 300 #/".

The measurement of the volumes of gaseous mixtures released from solution upon decrease of pressure has several disadvantages. The composition of this gas will not be the same as that of the original gas used in preparing the solution. The complete recovery of dissolved gas is uncertain. It, therefore, seemed advisable to attempt the direct measurement of gas dissolved.

The general plan developed is briefly as follows: The gas from the field is brought to the laboratory in cylinders under pressure. The gas is measured by a suitable method and compressed by a mercury displacement pump operated by compressed air. From the pump the gas passes into a saturation chamber where it is brought to equilibrium with the oil.

The use of this apparently simple process necessitates the consideration of several complications. Since the oil does not entirely fill the saturation cell nor the tube connecting it with the pump, the volume of gas required to bring this free space to any given pressure must be determined. This was accomplished by successively inserting two steel slugs of known volume into the saturation cell and determining for each slug the amount of gas required to bring the system to a given pressure. From this data the amount of gas required to bring any portion of the system to a given pressure can be calculated. Knowing the total amount of gas admitted to the cell, the amount of gas occupying the free space over the oil, (in the future this will be called "initial volume") and the quantity of oil in the chamber, the amount of gas actually dissolved in the oil can be computed easily. The actual calculation is not quite as simple as this, for the volume of the oil increases upon the solution of gas, thus changing the initial volume. The thermal expansion of the oil must also

be taken into account in a determination of the initial volume at other than room temperature.

In carrying out the above method several difficulties were encountered. The composition of the gas from the storage cylinder was found to vary as gas was removed from it. This was due to the liquifaction of a portion of the gas at the initial pressures existing in the cylinder. The variation was overcome by heating the cylinder above the critical temperature of most of the constituents.

The gas was measured by introducing it into a closed chamber and noting the fall in pressure as gas was drawn off to the pump. The temperature was maintained constant, the decrease in pressure thus giving a direct indication of the amount of gas removed. Since the chamber system was calibrated under conditions existing in use, no radical assumptions or gas law corrections are involved in the measurements. Provision was made for refilling the chamber whenever the pressure became too low for efficient pumping.#

# A more detailed description of this method of measuring gases under pressure can be found in the thesis of F. P. Stapp C. I. T. 1930. The pump is essentially a closed U tube, which is half filled with mercury (See Fig. 6). The gas is admitted over the mercury and forces it into the other leg of the tube. When the desired amount of gas has been admitted from the measuring chamber ("reservoir cell") the gas inlet valve is closed and the mercury forced back into the gas leg by admitting compressed air to the top of the other leg. The gas outlet valve is now opened allowing the gas to pass into the saturation cell. This process is repeated until the desired pressure is reached. The top of the gas leg of the pump and the line connecting it to the saturation cell are heated to 105°C to prevent the liquifaction of a portion of the compressed gas.

The saturation cell is located in a variable temperature thermostat and connected to the pump by means of a small tube. The cell is so arranged that it can be shaken as gas is admitted. The pressure on the cell is determined by means of a Bourdon gauge connected to the blow-off line of the cell by means of a mercury trap. This development was necessary to prevent condensation of portions of the gas in the tube of the gauge.

#### Description of Apparatus

Due to the use of the mercury displacement pump, it was undesirable to use brass or copper in the gas system of the apparatus. The tubing finally used was Shelby seamless steel, one eighth inch outside diameter. The fitting developed for use with this tubing ("Standard Fitting") is shown in cross section in Fig. 1. In earlier models the stem was made of brass, but due to amalgamation, several swelled to such an extent that it was necessary to drill them out of the steel follower. It is desirable to have (flats) on the stem to allow one to prevent the tubing from twisting on tightening the follower. The steel tubing was silver soldered to the stem, this being far superior to the use of soft solder, which fails after the tube has been bent or twisted a few times.

The conditions to be met by suitable valves are quite severe. They must be gas tight and have such throttling characteristics as to permit control within 0.2 c.c. (measured at 1 atm.). The packing (if any is required by the design) must be gas tight and at the same time not require an excessive amount of torque to turn the stem. They must be constructed of material which is not affected by any of the



Parts Made of Steel

19.1

Needle Valve Parts Made of Steel Except Needle



conditions to which it is exposed. They must also operate satisfactorily over an extended temperature range.

The general design was taken from that used by the Fixed Nitrogen Research Laboratory. To this was added a monel metal point held in the steel stem by means of a follower. A cross section of the valve is shown in Fig. 2. This swivel point construction prevents scoring of the point. The valves were packed with a lead amalgam, prepared from metallic packing and mercury. This amalgam formed an excellent seal and was also a good lubricant. Other than adding a little mercury to the packing and tightening the follower at intervals the valve required no attention and worked very well over a rather wide temperature range,  $(60^{\circ}F - 220^{\circ}F)$ . In parts of the system where quantitative results were not required Metric and special elbow needle valves were employed.

The reservoir cell, shown in cross section in Fig. 3, needs little explanation. It was designed for use at 3,000 #/", but is now only used at pressures under 300 #/". The upper standard fitting is connected to the gas inlet value (D) (See Figures 4 and 3) and to a 300# steel tube Bourdon gauge (F). The lower fitting

Reservoir Cell





RESERVOIR THERMOSTAT

- R Calibrating buret
- M Saturation cell gauge
- V Gauge trap
- F Reservoir gauge
- C Reservoir Cell
- D Reservoir refill valve
- B Gas storage cylinder

- Fig. 4 -

is connected through gas inlet valve (E) to the top of the pump. The cell is supported by a wooden bracket in an air thermostat which is maintained at 35°C.

Since the gases used deviated widely from the gas laws and the indications of a Bourdon gauge are not entirely regular, some method of calibration is necessary. A gas buret of the usual type holding about 321 c.c. was used (See Figure 4). The buret was located in the thermostat along with the reservoir and was connected to it through a needle valve.<sup>#</sup>

As the pressures used are low (300 #/" max.) and a sensitive test gauge is used for indicating the pressure, a plot of gauge reading against volume removed from the cell is almost a straight line which makes interpolation easy. By the use of a calibration curve of this nature it is a simple matter to determine the amount of gas admitted to the pump between any two given pressure readings. It is necessary to recalibrate at intervals as the characteristics of the gauge change slightly with use. Also a new calibration is necessary for each gas studied.

# A detailed description of the method of calibrating a chamber of this nature can be found in F. P. Stapp's C. I. T. 1930. Many parts of the pump are the same as when it was used by Swartz,<sup>#</sup> but several changes were made since it became necessary to pump gas quantitatively. Views of the pump assembly are shown in Fig. 6 and 5. The position of the mercury is determined by means of three contacts inserted at intervals in the gas leg of the pump. The floweof mercury is controlled by means of valve (I) located between the chambers of the pump.

Since the gas was measured before admission to the pump, it became imperative that the mercury be returned to the same height each time. To insure this a steel cylinder was attached to the top of the gas leg. (In the future this cylinder will be referred to as "pump top"), (See Fig. 5 and 7). To the upper portion of this cylinder were attached the gas outlet and inlet valves (E and J). In the upper end of the cylinder was inserted a removable plug containing a contact (See Fig. 7) to the inside end of which was attached a 3" portion of 6H pencil carbon. The rod was connected to the core of the contact by means of a split sleeve. The carbon was held concentric with the cylinder by

# Ph. D. Thesis C. I. T. 1930.



MERCURY DISPLACEMENT PUMP

- Fig. 5 -



18

PUMP AND SWITCH PANEL

S Gas leg of pump

K Air pressure gauge

I Mercury control valve

H, and H, Air inlet valves

0,,02,03 Indicating lights

L Air exhaust valve

T Air storage cylinders

Fig. 6



- Fig. 7 -

means of a washer in the lower end. It was found necessary to nickel plate the upper end of the graphite rod in order to reduce the contact resistance between it and the split sleeve. It was also necessary to remove most of the wax from the rod, thus rendering it quite fragile.

The outside of the cylinder was electrically heated to 105 C. The heater was built of asbestos paper, #30 chromel-A-wire and bakelite cement. The temperature was determined by means of a thermometer inserted in a well attached to the cylinder. The entire surface was well lagged to prevent localized cooling. The lagging was so applied as to permit easy inspection of the heater and valves.

By noting the decrease in the apparent resistance of the carbon rod, the position of the mercury in the pump top could be determined within one sixteenth inch or less. Since the inside diameter of the cylinder was only three sixteenths of an inch the variation in the volume displaced by the mercury was very small, (2 c.c. of gas measured at 1 atm.).

The contacts used in the pump caused the most difficulty because the mercury would short the contact with even the most minute leak. The type finally developed is shown in cross section in Fig. 7. This direct compression bakelite seal has given no trouble. Linen packing and cements were tried, but all gave trouble whenever the temperature was changed to any marked degree.

Elbow type needle valves (See Fig. 5) were used on the air chamber of the pump as small leaks were not serious. Two air storage cylinders T and T (See Figures 9 and <sup>(C)</sup>) were used in order to decrease the frequency of refilling. (The compressed air was obtained from a four stage compressor used at the liquid air plant located in the Norman Bridge Laboratory.) A Bourdon gauge was connected to the air chamber aiding manipulations to a great extent.

The heater for the tubing, connecting the pump with the saturation cell, was constructed of asbestos paper, #30 chromel-A-wire and bakelite cement. It consumed about 150 watts. The temperature was determined by a thermometer inserted in a well soldered to the line. Both the pump top and the line were heated to  $105^{\circ}$  C.

The air thermostat (See Figure 4) in which the reservoir, gauges and calibrating equipment were located was constructed of two thicknesses of one half inch celotex separated by a two inch air space. It was 48"X30"X20" inside. The air was kept in circulation by a motor driven fan located at the top and back. The heat was supplied by a 500 watt "glocoil" heater, controlled by a bimetallic strip regulator.<sup>#</sup> A rheostat was also placed in series with the heater allowing the relative lengths of the heating and cooling cycles to be controlled. Double glass windows were inserted in the front to permit reading of the gauges and calibrating apparatus.

The saturation cell is shown in cross section in Fig. 8 and needs little other explanation. The two connections in the top were used for inlet and blowoff respectively. The blow-off was by a separate line to prevent contamination of the incoming gas with oil carried into the line when pressure was released. The cell was held by a strap iron clamp at the end of a six inch bell crank. The shaft of the crank protrudes through the thermostat walls and was given an oscillating motion of about 80° some 45 times a minute by an electrically driven linkage. To allow for this motion both the inlet and blow-off lines were made in the form of a helix. Five turns

# R. D. Pomroy Ph. D. Thesis C. I. T. 1931.



- Fig 8 -

were ample to allow a movement of 90° without creating undue stress in the steel tubing.

The action of the shaker was very good, for equilibrium could be reached with a medium viscous crude in less than one minute. If the oil was very viscous however the action of the shaker was of little value in speeding saturation.

In replacing samples the standard fittings at the top of the cell were removed, the clamp holding the cell to the bell crank was loosened and the saturation cell removed from the thermostat. It was then placed in a vice and the cap screws and top removed. The cell was cleaned and was then ready for another sample.

The thermostat in which the saturation cell was placed was built by the Carrier Engineering Corporation, Tycos air controlled electric heating was used. The temperature variations were not over 0.3°C.

The general plan of the apparatus can be seen from Fig. 6. The pump and switch panel were located beneath the reservoir thermostat (See Figure 6). The saturation cell and thermostat were to the left of this, while the gas storage cylinder with its heater was to the right of the pump. The air cylinders, which were carried on a two wheel hand truck, were at the back of the pump.

#### General Procedure

In the following discussion the notations used in describing the operations will refer to the general flow sheet of the apparatus in Figure 19, unless otherwise noted.

The gas sample (B) was allowed to come to temperature (about 70° C). This usually required about two hours, but as the steam was turned on at an early hour this caused no delay in the operation of the equipment. A calibration of the reservoir by means of the gas buret and initial volume determinations are assumed to have been made beforehand. While the storage cylinder was heating, the sample of oil was weighed into the saturation cell (A). Such a quantity of cil was used that the oil came within 2 c.m.of the top of the cell, the actual distance being determined with a hook gauge. The top was then bolted on the cell and the whole placed in the thermostat. The gas inlet and blow-off lines were next attached and the whole apparatus allowed to come to thermal equilibrium. The time required varied with the temperature at which the determination was made, being a maximum of about three hours when working at 200 F.

After both the storage cylinder (B) and the satur-

ation cell (A) were up to temperature, gas was admitted from (B) into the reservoir (C) by means of valve (D). When gauge (F) had become steady a reading was taken. Gas was then admitted from reservoir (C) into the pump (S) through valve (E), the amount of gas admitted being measured by the fall in pressure in the reservoir read directly from gauge (F). Valve (E) was then closed and air inlet valve (H) was opened. Mercury control valve (I) being opened gradually, the inflowing mercury compressed the gas in the gas leg (S). Gas outlet valve (J) was then opened allowing gas to flow into the saturation cell, the shaker motor having been started. As the mercury rose in the gas leg of the pump the respective lights  $(0, 0_2, 0_3)$  would go on as the mercury reached their level. More and more air was admitted from the air tanks  $(T, , T_1)$  by means of air inlet valves (H., H.) maintaining an excess pressure on the air side. As the mercury approached the top of the gas leg, the differential pressure across the mercury control value (I) was reduced to about 200 #/<sup>N</sup>. After the top light (0,) flashed, the mercury was admitted cautiously until a movement of the galvanometer indicated that the mercury had reached the lower end of the carbon rod. The mercury was then admitted slowly until the bridge was in balance, showing that the mercury was at a





•

В	Gas storage cylinder	I	Mercury control valve
C	Reservoir cell	Η,	,H2 Air inlet valves
D	Reservoir refill valve	G.	Air exhaust valve
F	Reservoir gauge	т,	,T <sub>1</sub> Air storage tanks
E	Gas inlet valve	A	Saturation cell
J	Gas cutlet valve	L	Blow-off valve
S	Gas cylinder of pump	Μ	Saturation cell gauge
0, ,	,0,,0, Indicating lights	K	Air cylinder gauge
	- Fig.	9	324 2

predetermined height in the "pump top". The mercury control valve (I) was completely closed, as was the gas outlet valve (J). The air exhaust valve (G) was then opened. The pressure on the saturation cell was determined from gauge (M) and when this became constant the shaker was shut off and the pressure recorded. The time required to reach equilibrium varied widely depending to a great extent on the viscosity of the oil. However it was rarely over five minutes and in most cases less than one minute.

Next, more gas was admitted from the reservoir (C) and it was compressed as before making sure that the pressure in the gas leg of the pump was in excess of that in the saturation cell (A) before gas outlet valve (J) was opened. The pressure existing in the gas leg was determined by allowing the air to compress the gas until the gas and air pressure were in equilibrium and then reading the air pressure from gauge (K). The cell was again shaken as the gas was admitted from the pump (S) and another set of readings taken. More gas was admitted from cylinder (B) whenever required.

The process described above was repeated until the equilibrium pressure in the saturation cell reached the maximum desired. Since the amount of gas admitted to the pump was measured and the corresponding equilibrium pressure in the saturation cell was observed, we have a complete curve of the total volumes admitted against the equilibrium pressures. These values required correction for initial volume before the true amount dissolved in the oil could be determined. The time required for a run as described above was about an hour and a quarter for a pressure range from atmospheric to 2,500 #/". The data was always plotted as it was obtained and thus a check on the operation of the equipment was constantly available.

After the run was completed the blow-off valve (L) was opened and the gas along with some entrained oil was blown out of the saturation cell. The cell was removed from the thermostat, opened, cleaned and allowed to cool. It was then ready for another sample.

As mentioned the data obtained from a solubility run required correction for the free volume over the oil ("Initial Volume"). Since the volume of the oil changed when gas was dissolved in it, it was necessary to determine the amount of gas that would be required to bring any portion of the saturation cell, along with the accompanying tubes and trap, to any pressure in the range used. This was accomplished by the use of two steel slugs, one of which occupied most of the volume of the saturation cell and the other about half filled the cell. They were one inch and two inches long by two inches in diameter respectively. The volumes of these slugs were accurately determined by water displacement. These slugs were successively placed in the saturation cell and runs similar to that described above made. The difference in the amount of gas used in the two runs is obviously that used in bringing space equal to the difference in volume of the two slugs up to the given pressures. From this data was calculated the volume of gas required to bring any given portion of the saturation cell and system to any required pressure. These initial volume runs were of necessity made with each different gas used and at each temperature studied with these gases.

#### Calculation of Results

The actual calculation of the true solubility is not as simple as it first appears as there are several factors which must be taken into account in such a calculation. Change in volume of the oil due to dissolved gas and thermal expansion of the oil are the only ones of major importance however. Due to the design of the cell increase in volume of the cell due to pressure was negligible. The compressibility of the oil was also neglected in the following calculations.

The increase in volume of the oil was found to be very nearly proportional to the amount of gas dissolved". The coefficient of thermal expansion was measured and was assumed to be a constant over the range studied. The correction for the thermal expansion was first applied to the volume of original oil actually in the cell. The total volume of the entire system was next calculated from initial volume data. The free volume over the oil was obtained directly by subtraction. By again referring to the initial volume and saturation curves the amount of gas apparently dissolved in the oil was obtained. But due to the expansion of the oil due to dissolved gas, the free volume was actually less than this calculated value by the increase in volume of the oil. Now, if the increase in volume of the oil were determined on the basis of apparent amount of gas dissolved, the actual increase in volume of the oil could be directly calculated and approximation avoided.

Having the true volume of the oil after the gas had been dissolved in it, it was possible to determine the true free volume over the oil and from this the true solubility of the gas in the oil at that pressure

# Thesis. E. S. Hill C. I. T. (1931)

and temperature. This calculation was carried out for each pressure at which the saturation was measured.

The first work that was done with the apparatus was on samples of Kettelman Hill's oil and gas. It has been chosen as an example, as change in volume data was determined for these samples. This data on change in volume on dissolving gas in the oil is believed to be a good approximation, but cannot be entirely relied upon. The samples chosen were those from Well # 38 of the Standard Oil Company of California. This oil was very light in color and had a density of 60.8° A.P.I. and a very low viscosity. The gas from the same well gave the following analysis:

Methane	80.13%
Ethane	6.91
Propane	5.43
Isobutane	1.32
n-butane	2.72
Isopentane	0.39
Heavier	3,10

The actual calculation of one value is given below: Data

Volume of oil in the cell @ 75°F 88.18 c.c. Change in volume of the oil per c.c. of apparent gas dissolved 0.0019 Coefficient of thermal expansion 0.000612 Volume of entire system 155.20 c.c. 140°F Temperature of run 1953 #/" Pressure (gauge) Initial volume (with slug) @ 1953 #/" 6605 c.c. Volume of slug 112.00 c.c. Total volume of gas admitted 18055 c.c.

#### Calculations

Correcting for thermal expansion: 0.000612 x 65 x 88.18 = 88.18 91.68 c.c. Determining uncorrected free volume: 155.20 - 91.68 = 63.52 c.c. Free volume. Volume of gas apparently over the oil:

 $\frac{63.52 \times 6.605}{(155.20 - 112.00)} = 9,740$  c.c. of gas

Apparent solubility:

18,055 - 9,740 = 8,315 c.c. of gas dissolved.

The increase in volume of the oil due to dissolved gas: 8,315 x 0.0019 = 15.80 c.c. increase The true volume of the oil in the cell after the gas is dissolved:

 $91.68 \neq 15.80 = 107.48$  c.c. of oil The true free volume over the oil:

155.20 - 107.48 = 47.72 c.c. of space The actual amount of gas in the free space:

 $\frac{47.72 \times 6.605}{(155.20 - 112.00)} = 7,308$  c.c. of gas

The actual amount dissolved:

18,055 - 7,308 = 10,747 c.c. of gas dissolved. Converting to comparable units:

> <u>10.562 x 51.2</u> = 691.2 cubic feet of gas per 88.18

barrel of original oil.

The remainder of the values in the following table (See Fig. 10) were obtained in similar manner, as were those for 170°F and 200°F. The results are shown graphically in Fig. 11.

The results shown in Fig. 11 are to serve only as an illustration of the performance of the apparatus. During the year the solubility of a sample of scrubbed Santa Fe Springs gas was determined in 12 representative crudes at 80,100,120, and 140°F. Data covering the

# SAMPLE CALCULATION Fig.10

Pres.	Total Vol.	Apr.	Apr.	Inc. in Vol.	Space over	Act.	True Solb.	Selb. Cu.ft.
10000					011			/
163	1460	698	762	1.4	62.07	685	775	49.7
394	3595	1747	1848	3.5	60.00	1648	1947	124.7
555	5075	2535	2540	4.8	58.69	2339	2736	175.4
767	7090	3558	3532	6.7	56.80	3178	3912	250.8
979	9120	4602	4518	8.6	<b>549</b> 2	4060	5060	325.0
1313	12170	6240	5931	11.3	52.24	5140	7030	452.8
1637	15200	7990	7210	13.7	49.80	6260	8940	573.1
1953	<b>180</b> 55	9740	8315	<b>1</b> 5.8	47.72	7308	10747	691.2

# This value was used in detailed sample calculation



Figure 11



- Fig. 12 -

change of volume resulting from change in temperature and on dissolving gas in the oil are to be available as a result of work being carried on at the U.S. Bureau of Mines under the auspices of the American Petroleum Institute. For this reason no attempt has been made by us to obtain such results and until such time as they are available, no accurate calculations of the solubility values can be made. Therefore only a single case has been cited in this report.

## Acknowledgments

A great deal of credit is due Mr. E. S. Hill whose aid in construction of the apparatus was invaluable. Dr. W. N. Lacey's helpful suggestions and aid in obtaining equipment and materials has contributed much to the success of the apparatus. This research has been made possible by a grant of funds made available by John D. Rockefeller and the Universal Oil Products Company and has been carried on as a part of Project #37 of the American Petroleum Institute. To these and several others who have aided in the work the author wishes to express his sincere appreciation.

### Conclusion

A method has been developed and an apparatus perfected for measuring the solubility of gases in liquids for wide temperature and pressure ranges. Application of this apparatus to determination of the solubility of natural gas in petroleum oils has been carried on. The results obtained show very satisfactory reproducibility. Numerous solubility data have been obtained but final values cannot be reported until other pertinent data is available. It is hoped that a wide extension of the present work will be possible in the near future.